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Cure Characteristics of Metal Particle Filled DGEBA/MDA/SN/zeolite Composite System for EMI Shielding

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Abstract

The cure characteristics of metal particle filled DGEBA/MDA/SN/zeolite epoxy resin composite system for EMI shielding were investigated by dynamic DSC run method and FT-IR spectroscopy. As the heating rate increased, the peak temperature on dynamic DSC curve increased because of the rapid cure reaction. From the straight line of the Kissinger plot, the curing reaction activation energy and pre-exponential factor could be obtained. As the post-curing time at 150 ℃ increased, the glass transition temperature or the thermal stability increased. When the post curing time is too long, the system filled with metallic Al particle can be thermally oxidized by the catalytic reaction of metal filler and the thermal stability of the composite for the EMI shielding application may be decreased.

Key Words : EMI shielding, Epoxy resin, Metal particle, Zeolite filler, DSC, Cure kinetics

1. Introduction

The electric and electronic industries have been rapidly developed over the last 10 years. The size and weight of the electric components decreased by using polymeric materials in substitution of conducting metals for the component housing. The general polymers are transparent to the electromagnetic wave, so the electromagnetic interference(EMI) phenomenon is a new problem encountered with the application of polymeric material for electric and electronic parts and equipments[1].

One of the solutions for these problems is incorporating the polymeric materials with conducting metallic fillers in types of particle, flake, fiber, etc. The insulating polymers filled with conducting fillers have many industrial applications in electricity as EMI shielding, antistatic materials, abrasive resistance material, PTC, and so on[2,3].

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In this study, the natural zeolite, which is abundant in our country and didn't attract the public interest because of the low cognition and bad industrial condition, was filled with metal particles into the polymeric material DGEBA/MDA/SN epoxy resin system for the application of EMI shielding[4]. The properties of polymer composites depend not only on the mixing ratio of components but also on the cure conditions. The reacting mixture was heated by DSC and the thermograms were analyzed by using a kinetic model for the investigation of cure characteristics of the composites. Also, the thermal properties of glass transition temperature(T_g) and cure reaction activation energy(E_a) were measured.

2. Experiment

The epoxy resin used in this study was DGEBA(diglycidyl ether of bisphenol A, Epon 828 grade) with EEW, MW and viscosity of 188, 385 and 11,000-14,000 cps(25 ℃), respectively. 30 phr of MDA(4,4'-methylene dianiline) was mixed with epoxy resin as a cross-linking agent. SN(succinonitrile) was added as a reactive additive. The epoxy resin was filled with 20 phr of clinoptilolite type zeolite(325 mesh, 20.07 ㎛)

and Al(Hayashi Pure Chem. Ind.). The zeolite particle fillers were dehydrated at 100 ℃ vacuum oven before mixing with the resin. The components were mixed at 80 ℃ and cured for 1.5 hr. The samples were post-cured for 7 hr at 150 ℃.

DSC curves of the mixture and cured systems were studied by using Solomat DSC calorimeter at various heating rates. To study the cure kinetics by dynamic DSC analysis, 2~3 mg of the mixture was placed in DSC Al pan and DSC analysis was performed at the heating rates of 3, 5, 10 and 20 ℃/min. It was carried out at the nitrogen atmosphere of 100 ml/min flowing rate to prevent the thermal oxidation process during the cure reaction at high temperature. Curing characteristics were investigated by FT-IR (Bomem MB-104) equipped with MCT detector and ATR accessory.

3. Results and Discussion

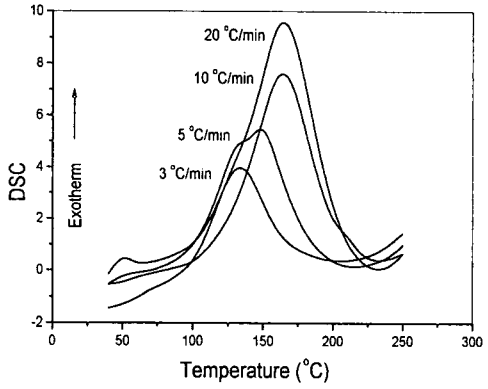

Fig. 1. DSC curves of DGEBA/MDA/SN/zeolite/Al composite system at various heating rates by dynamic DSC run method under N_2 inert gas condition.

Fig. 1 shows the dynamic DSC curves of the DGEBA/MDA/SN/zeolite/Al epoxy composite system at the different heating rates of 3, 5, 10 and 20 ℃/min. As the heating rate increased, the cure reaction of epoxy resin composite system took place rapidly in a short time, so the exothermic peak temperature increased. Each curve shows only one exothermic peak due to primary amine-epoxide reaction, secondary amine-epoxide reaction, catalytic reaction and epoxy-hydroxyl reaction.

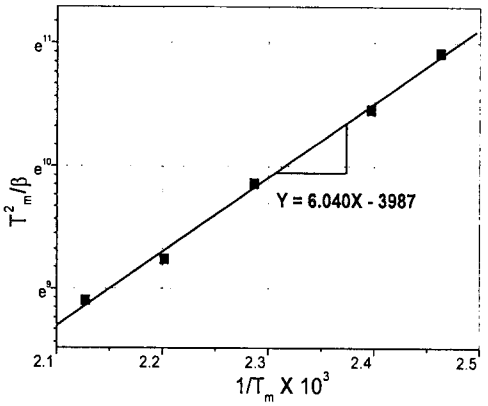

Fig. 2. Plot of $-\ln(\beta/T_m^2)$ vs. $1/T_m \times 10^3$ by Kissinger equation for DGEBA/MDA/SN (10 phr)/zeolite(20 phr)/ Al(10 phr) epoxy resin composite system.

From the DSC peak data on Fig. 1, the cure reaction activation energy and pre-exponential factor are obtained by using Kissinger expression, which is

$$-\ln\left(\frac{\beta}{T_m^2}\right)=\frac{E_a}{R}\cdot\frac{1}{T_m}-\ln\frac{AR}{E_a}$$

where, β : heating rate, T_m : temperature at the peak value of the DSC curve, E_a : cure reaction activation energy, A : pre-exponential factor, R : gas constant[5]. A plot of $-\ln(\beta/T_m^2)$ as a function of $1/T_m$ gives activation energy from the slope of the straight line as shown in Fig. 2. The activation energy and pre-exponential factors can be obtained from the slope and the y-interception, respectively. The thermally curing activation energy was 52.216 kJ/mol.

The thermal properties of epoxy resin composite system depend on the mixing ratio of the components and curing conditions.

DGEBA/MDA/SN(10 phr)/zeolite(20 phr)/Al(10 phr) was cured at 80 ℃ and then post-cured at 150 ℃ for various periods from 0 to 7 hr. As the post-curing time at 150 ℃ increased, the exothermic peak by the curing reaction lowered and the glass transition temperature appeared above room temperature as shown in Fig. 3. The glass transition temperature of the system cured at 80 ℃ for 1.5 hr and post-cured at 150 ℃ for 7 hr was 125 ℃. The addition of mineral fillers can shift the transitions to the right or to the left depending on the constituting components. The DSC curves of the cured system did not exhibit significant endotherms on heating above the glass transition temperature. This fact supports the proper curing condition.

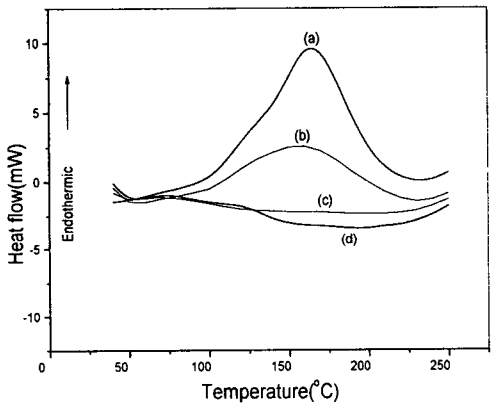

Fig. 3. Effect of curing condition on the DSC thermograms of DGEBA/MDA/SN(10 phr)/ zeolite(20 phr)/Al(10 phr) epoxy resin composite system. (a) mixture (b) 80 ℃ for 1.5 hr (c) 80 ℃ for 1.5 hr and 150 ℃ for 1 hr (d) 80 ℃ for 1.5 hr and 150 ℃ for 7 hr.

It is interesting to observe the influences of filler on the temperature of the β- transition which is due to some local segment motion in the chain[6]. The highly loaded fillers can affect the local motion of the polymeric main chains. As the post-curing time increased, the thermal stability(T_g) increased. When the system is over-cured for longer than 7 hr, the transition temperature can be decreased by the catalytic thermal-degradation reaction of metallic Al particle in the thermally oxidizing degradation process.

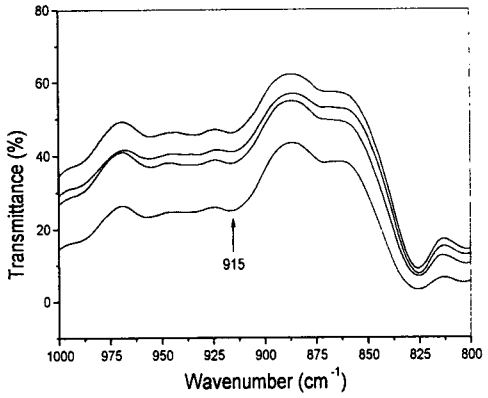

Fig. 4. FT-IR spectra of post cured DGEBA/MDA/SN(10 phr)/zeolite(20 phr)/ Al(10 phr) epoxy resin composite system.

The FT-IR spectra of Al particle filled DGEBA/MDA/SN/zeolite system showed lots of noise, so that it was difficult to analyze all the spectra. The metallic Al filler reflects the electromagnetic wave, so that the Al is usually packed with other kinds of fillers such as carbon black, carbon short fiber, metal coated fibers, and so on which can absorb the electromagnetic wave and transit the energy into the thermal heat-loss[7]. To understand the cure characteristics of metallic aluminum particle and inorganic mineral zeolite particle filled epoxy resin composite system, the transmittance peak of epoxide ring at 915 cm^{-1} was observed by using FT-IR spectroscopy. As the curing time increased, the epoxide rings were opened and participated in the curing reaction. When the system was secondary cured longer than 1 hr at 150 ℃, all the epoxides were reacted and the increase of transmittance was not detected as shown in Fig. 4. But the thermal stability increased because the system was more densely packed as the system was post cured.

4. Conclusions

The cure characteristics of metal particle filled DGEBA/MDA/SN/zeolite epoxy resin composite system for EMI shielding were investigated by dynamic DSC run method and FT-IR spectroscopy and the following conclusions were obtained. As the heating rate increased, the DSC peak temperature increased because of the rapid cure reaction. The curing reaction activation energy from the straight line of the Kissinger plot was 50.216 kJ/mol. As the post-curing time at 150 ℃ increased, the glass transition temperature increased. When the post curing time is too long, the system filled with metallic Al particle can be thermally oxidized by the catalytic reaction of metal filler and can decrease the thermal stability of the composite.

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